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THE EFFECT OF LIQUID--LIQUID PHASE SEPARATION
OF GLASS ON THE PROPERTIES AND CRYSTALLIZATION
BEHAVIOR

Li Jia Zhi

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16. Abstract A theoretical discussion is given of the phase separation mechanism of amorphous materials. This includes nucleus growth, spinoidal decomposition, and nuclei agglomeration and coarsening. Various types of glass are analyzed.					
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THE EFFECT OF LIQUID--LIQUID PHASE SEPARATION OF GLASS ON THE PROPERTIES AND CRYSTALLIZATION BEHAVIOR

Li Chia Chih^{*}

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I. INTRODUCTION

Fifty years ago, Greig [1] indicated that there is an S-shaped liquid phase line in the BaO-BaO·SiO₂ system. This is probably due to the presence of a nonmixing substable Spinodal zone beneath the liquid phase line. The configuration and location of the Spinodal zone were proposed. Since then this little noted phenomenon has developed into one of the important achievements in the fields of amorphous state physics and chemistry.

Greig's initial and ensuing studies were mainly concentrated on the phase separation from the stable phase above the liquid phase line. To glass researchers, the major interest is still focused upon the study of the glass forming zone, because the separation of the stable liquid phase lends itself to the formation of a layer or becoming turbid after the molten glass is cooled. This phenomenon can be easily observed by the naked eye or an optical microscope. Later, scientists shifted their attention to the investigation of the phase separation phenomenon from the Spinodal or unstable liquid phase below the liquid phase line, although in some instances there was no evidence of turbidity after cooling the glass, but the presence of a microphase separation zone was evidenced with the use of an electron microscope at high magnification. Sometimes it was required to go through proper heat treatments near the glass transition temperature prior to observation by electron microscope.

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^{**} Numbers in margin indicate pagination of foreign text.

Two favorable theories of glass structure were proposed in the early 30's--(a) homogeneous irregular network structure and (b) heterogeneous crystal structure based on the X-ray studies of amorphous materials. Again, in the 50's, a new concept appeared which shook the old theories-- that is, liquid phase separation is a common existing phenomenon in the glass forming system. This discovery is attributed to the development of the electron microscopy and its application to the study of the amorphous materials.

In the early 60's, Cahn [2] proposed a mechanism of Spinodal decomposition as one of the phase variation theories concerning glass liquid phase separation. He applied certain conditions of the concentration gradient. Through a Fourier transform, the calculation was made for the structure of the liquid phase separation in the mixable zone. The result showed that there are two phases connected together. The mechanism was verified through numerous experiments. Thus, the interest in studying liquid phase separation theory and its experiments gained further momentum.

In the mid 50's, Yin Zhi Wen and coworkers of this center had already begun to study the relationship between the phase separation zone and the properties of an $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system during their investigation of high silica glass. In the early 60's, Jin Zhen and Ming Si Kuei [3], in their study of $\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ microcrystalline glass without introducing any nucleating agent, had used liquid phase separation to interpret a crystallization process. Li Jia Zhi, et al. [4], in the study of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2$ microcrystalline glass, also discovered that the introduction of TiO_2 will not simply function as a nucleating agent. They further discussed the relationship between nucleation and glass phase separation. These pioneering works clearly showed our close attention to glass phase separation and early advances in this field. This study will not discuss much about the relationship between the phase separation and

structure of glass, since many review articles [5-7] are known /280
in this field. Instead, this article will concentrate on the thermodynamic aspect of glass liquid-liquid phase separation, dynamics consideration and morphology of phase separation. Special attention is placed upon the effect of liquid-liquid phase separation on physical-chemical properties and crystallization behavior, particularly on the nucleation.

II. THERMODYNAMICS CONSIDERATION OF A PHASE SEPARATION

Before discussing the thermodynamics of glass phase separation, the contribution made by Gibbs in theory and practice in this field must be discussed.

Gibbs [8] in his study of liquid phase stability, simultaneously proposed the effect of micro fluctuation of a stable phase and of composition or density on the stability of the liquid phase.

With respect to the first type of fluctuation, if the interfacial energy is positive, thus the original phase must be sub-stable or Spinodal. For the original phase to become unstable, a constant fluctuation is necessary in order to overcome a constant potential barrier to effectuate instability. This type of fluctuation is called nucleus. This will be discussed later as the nucleus growth mechanism. For the latter type of fluctuation, the necessary condition of liquid phase stability or Spinodal is that the chemical potential of a component should increase with density (concentration). The above two cases can be expressed by

$(\partial^2 G / \partial C^2)_{T,P} > 0$. In many glass systems, there is always one composition considered as a function of temperature T_c . The T_c is normally termed the critical temperature or consolute temperature. At this temperature, the stability condition of the original liquid phase is destroyed. That is, the condition that $(\partial^2 G / \partial C^2)_{T,P} > 0$

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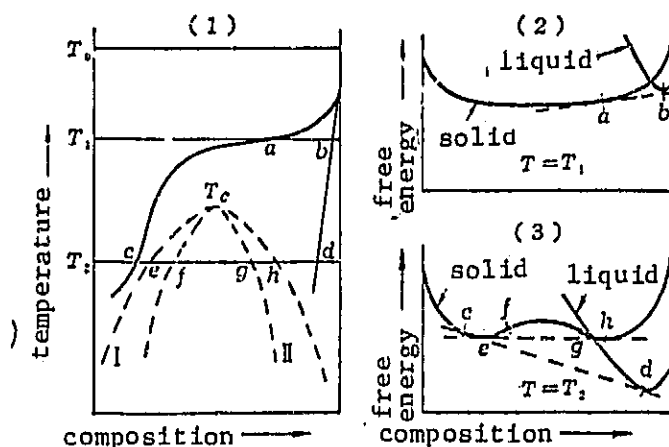


Figure 1. Binomial phase diagram and free energy--composition diagram

cannot be satisfied. Thus, a slight fluctuation of composition (density) will cause a phase separation without overcoming any potential barrier. The limit of substable or spinodal condition is $(\partial^2 G / \partial C^2)_{T,P} = 0$, called spinode. Its tracing locus is called spinodal. This type of phase separation mechanism is named Spinodal Decomposition [9].

For simplification, take a binomial system for example, under constant temperature and pressure, the free energy of formation of two components is a function of concentration. This relationship is shown in Figure 1.

The phase diagram and free energy--composition diagram in Figure 1 can be interpreted by two fundamental laws of phase diagrams constructed based on Gibbs free energy curves. These two fundamental laws are (1) under constant temperature, pressure and composition, the most stable state is with the minimum Gibbs free energy. (2) the composition of a liquid phase in equilibrium with the solid phase can be determined by a contact point of a line tangent to the liquid phase curve. The line is extended

from the solid phase free energy value at equilibrium. Figure 1 shows a phase diagram of existing spinodal nonmixable zones under a liquid phase line. Figures 1(2) and (3) are the respective free energy-composition diagrams at different temperatures. At temperature T_1 , the free energy curve of liquid is lower than the curve of mixing components and is convex toward the composition axis. Based on the first law, the free energy of liquid is lower than that of the unmixed components. Therefore, any composition of the single phase liquid is more stable than that of the unmixed component liquid. In other words, there is no phase separation. As temperature decreases to T_2 , the free energy of liquid goes up quickly. Due to smaller entropy for solid, its free energy goes up much more slowly. When temperature drops below the critical temperature, T_c , there is a limited nonmixability between the two component phases. That means a partial solubility between them. Based on the first law, the free energy-composition curve should be either concave or convex toward the composition axis as shown in Figure 1(3). Based on the second law, the composition of liquid and solid phases in equilibrium is determined by the respective contact points made by a common line tangent to both the liquid and solid free energy curves. A cusp made on the liquid phase free energy curve determines the composition of liquid at equilibrium.

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Cahn and Charles [10] first applied Gibbs criteria for the necessary conditions of a binomial system liquid phase stability to the study of an amorphous system. Apparently, $(\partial^2 G / \partial C^2)_{T,P}$ becomes a control equation. It can be classified into three categories: If $(\partial^2 G / \partial C^2)_{T,P} > 0$, a positive value, then the liquid phase is stable or spinodal; if $(\partial^2 G / \partial C^2)_{T,P} < 0$, a negative value, then the liquid phase is stable or spinodal; if $(\partial^2 G / \partial C^2)_{T,P} = 0$, at zero, then the phase lies on the border line of the above two states. In Figure 1(3), the value of $(\partial^2 G / \partial C^2)_{T,P}$ for the liquid phase lies between e and f, is positive and at f is zero. From f to g it is negative and at g it is zero again. Meanwhile, from g to h it is positive. Therefore, this system is spinodal from e to f and

becomes unstable from f to g. But from g to h it is spinodal again. The curve beyond e and h regions has $(\partial^2 G / \partial C^2)_{T,P} > 0$, thus the liquid phase is stable with respect to a phase change.

III. DISCUSSION OF THE DYNAMICS OF PHASE SEPARATION AND ITS MORPHOLOGY

On the basis of current knowledge of the dynamics of phase separation, the phase separation mechanism of the amorphous materials can be divided into three stages: (1) early stage of nucleus growth, (2) spinodal decomposition and (3) later stage of nuclei agglomeration and coarsening. Using the thermodynamics viewpoint as a starting point, the two phase separation zones can be used for the discussion of their dynamics problems. First, in the zone of $(\partial^2 G / \partial C^2)_{T,P} > 0$, it is spinodal with respect to the minimal composition fluctuation of a single phase liquid. The formation of a second phase depends upon the formation of a nucleus. Secondly, in the zone of $(\partial^2 G / \partial C^2)_{T,P} < 0$, it is unstable with respect to the minimal composition fluctuation of a single phase. Therefore, the phase separation is instantaneous and spontaneous.

1. Spinodal zone

Generally, the phase separation of the spinodal zone is achieved based upon the mechanism of nucleus growth. If an interface is not available in the single phase liquid, the formation of a nucleus should consume work in forming a new interface. The supercooling of the zone between the phase boundary and the spinodal boundary line makes the nucleus reach a certain degree of stability. The formation work, W , can be calculated from the properties of the two phases and the measurement of interfacial energy. Hillig [11] pointed out that the formation work is a sensitive function of temperature. Based on the equation of a homogeneous nucleus formation work, it can be approximately considered as $W = K / \Delta T^2$, where ΔT is the temperature below the phase boundary.

Accordingly, the W becomes infinitive above the phase boundary. This means that the formation of a new phase is impossible. Following a drop in temperature, that is, also an increase in supercooling, the formation work reduces quickly to provide a preferable environment for the formation of a new phase nucleus.

If an interface is present in the single phase liquid, as long as the interface is wetted by the liquid phase and has a constant contact angle, then the formation work of a nucleus, W , is still expressed by $K_1/\Delta T^2$. The only difference is $K_1 < K$.

When cooling reaches a spinodal boundary zone, this causes a change in the constant fluctuation property required for a shift from the spinodal liquid to the unstable liquid. The formation of a second phase nucleus does not possess a liquid droplet shape but merely a sort of composition fluctuation. On the spinodal boundary line, the nucleus formation work of this type drops to zero. Thus, the simple nucleation theory is limited by two boundaries between the neighboring phase boundary and the spinodal boundary line.

As long as liquid is located above the spinodal zone, the nucleation takes place as soon as the liquid temperature is brought down to the spinodal zone. Thereafter, the diffusion process controls its growth. The growth rate of a new phase is the rate of phase separation which is determined by the number of nuclei and the type of distribution. It is conceivable that the uniformly distributed nuclei and agglomerated nuclei have a different rate of phase separation.

2. Unstable zone

When the single phase liquid is cooled too fast as it passes through the spinodal zone and quickly reaches the spinodal boundary line area without any clear sign of phase separation, then its phase separation characteristics have been basically

changed. This is due to the nuclei being formed and the fresh growing point masses having suddenly stopped growth; instead they form the center of outward propagation with sine wave compositional variation. At the beginning stage, only the amplitude is increased. The two phases formed possess mutual penetration characteristics. This is different from a new phase formed by the nucleus growth mechanism. Figure 2 illustrates the characteristics of a phase separation by two different mechanisms.

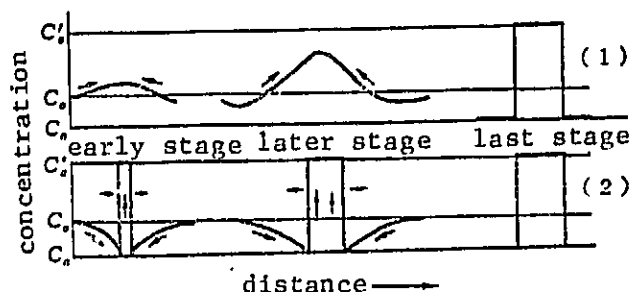


Figure 2. Spinodal decomposition

From Figure 2, when nuclei grow in a certain system, due to the formation of the nuclei, the concentration of the surrounding component is reduced. As a result, a diffusion takes place from the high concentration neighboring zone toward this low concentration zone.

This promotes the growth of any nucleus having its size larger than the critical dimension. During the spinodal decomposition, due to the concentration fluctuation, the concentration of certain components in the high concentration zone continues to increase before the second phase reaches its equilibrium composition. The surrounding concentration continues to drop until the equilibrium composition of a post phase separation is reached. The direction of diffusion is shown in the diagram by the arrows. If a certain component diffuses from a high concentration zone to the low concentration zone, this is named Positive Diffusion. Then the diffusion which occurs at the spinodal decomposition is called Negative Diffusion or "creeping diffusion". Since the two types of phase separation mechanisms are different, therefore, their morphologies are also different. Under normal mechanisms, the growth of a nucleus at a constant temperature is a function of time as the composition of a second phase is kept unchanged. There is a clear interface between the

two phases during the growth period. In the early stage, the second phase appears as tiny spheres with a low degree of linkage. However, it is quite different for the spinodal decomposition; prior to the equilibrium, the two phases continue to vary with time toward two composition extremes. In the early stage, the interface is not clear between the two phases. Until the very last stage, the two phases form a "looper" shape with a high degree of linkage.

Cahn and Charles [10] have discussed the dynamics of the spinodal decomposition of the glass liquid phase separation. One approach is to proceed with a quick cooling from the single phase zone, then incubate in the spinodal boundary zone. At a supercooling temperature, ΔT , 10% lower than the spinodal boundary temperature, the amplitude of fluctuation increases at an accelerated rate (typical wavelength 30-100 Å). Under this condition, the decomposition proceeds very quickly. Even with moderately high viscosity, it takes less than one second. At a much lower incubating temperature, due to a slowdown in diffusion rate, there is no phase separation appearing. Another dynamic approach is a quick cooling from a single phase without incubation. In order to avoid a complete phase separation, if the diffusion coefficient, D , of the molten body is $10^{-19} \text{ m}^2 \text{ sec}^{-1}$, then the cooling rate should be 1°C/sec . If D is $10^{-16} \text{ m}^2 \text{ sec}^{-1}$, then the cooling rate is 1000°C/sec . A different structure of phase separation may be obtained with a different rate of cooling.

It must be pointed out that the mechanism of phase separation cannot be solely judged by the morphology. Haller [12], in his study of the dynamics of the alkali metal borosilicate molten liquid-liquid nonmixable micro phase rearrangement, has pointed out that the mutual linkage structure of the phase separation may be from the conventional mechanism of nucleus growth. Since the dispersed liquid droplets of the liquid phase separation system do not possess the minimum surface free energy, therefore, they are thermodynamically unstable.

They tend to reduce the interface of the two unmixable phases. It is likely that agglomeration may occur in the low viscosity molten body. Haller called this the phase separation of the nuclei growth and agglomeration mechanism. Hopper and Uhlmann [13] supported Haller's observation. They presented four types of agglomerated models to explain that the nuclei growth of the dispersed liquid droplets may be agglomerated within a reasonable length of time without an interfering effect between the point masses, contrary to Goldstein's proposal.

When the fundamental phase possesses a high degree of saturation under constant temperature, the growth process of the second phase with a droplet shape is dependent upon long range diffusion. The relationship between the average radius of liquid droplet \bar{r} and time is $\bar{r}^3 \propto t$. However, when the composition of the fundamental phase and that of the droplet shape second phase is near equilibrium, then the growth of liquid droplets depends upon a coarsening effect. This means that the growth of large liquid droplets is dependent on the dissolution of smaller droplets. The related equation of the average radius of a liquid droplet with the increment of time is expressed by

$$\bar{r}^3 - \bar{r}_0^3 = \left(\frac{8}{9} \right) \left(\frac{\sigma}{RT} \right) DC_m V_m t$$

where \bar{r}_0 : average radius of a liquid droplet at the beginning of coarsening; σ : interfacial energy; D : diffusion coefficient; C : average concentration (g mole/m³) of solute in the fundamental system; V_m : g mole volume of the liquid droplet phase. The number of liquid droplets decreases with the increment of time. The relationship can be expressed as $N_v \propto t^{-1}$.

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It is worth mentioning that the system composition is an important factor in determining the phase separation structure. Seward III, et al. [14], in the study of the BaO-SiO₂ system found that different phase separation structures can be obtained from varying system compositions. When the composition is 0.04 BaO-

0.96SiO_2 , which is located in the middle of the mixable zone with high silica content, one of the phases has a small volume fraction with the droplet shape. As the composition shifts to $0.1\text{BaO}-0.9\text{SiO}_2$, it is located in the middle of the mixable zone with high volume fraction of both phases. As a result, the two phases form a high degree of linkage structure. Again, as the composition migrates toward another side of the mixable zone, on the high BaO side ($0.24\text{BaO}-0.76\text{SiO}_2$), one of the phases will possess a small volume fraction resulting in a droplet structure. The results are shown in Figure 3 with different morphologies of the respective phase separations.

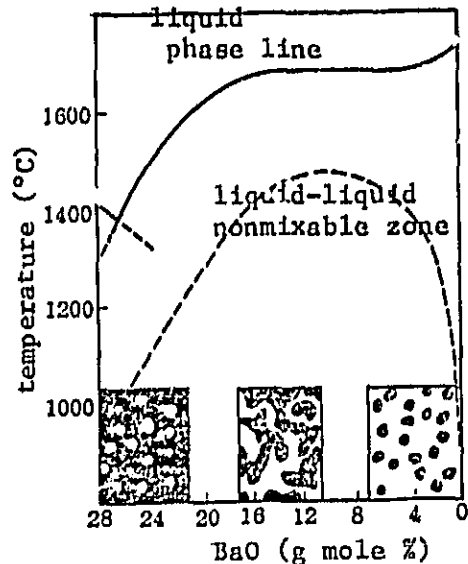


Figure 3. Phase diagram of barium silicate and nonmixable zones

Generally, what we observed is that one type of liquid droplet phase distributes in another homogeneous base system. However, in some systems, there are more than three micro phases being observed. This is typical of the $\text{BaO}-\text{B}_2\text{O}_3-\text{SiO}_2$ system with six micro phase structures.

It is known that the unmixable zone below the liquid phase line also appears in the phase diagram between two stable compounds. If the cooling rate is sufficiently slow, the composition of two separated phases is very similar to that of the stable compounds. If the cooling rate is very fast, then the degree of similarity will be slightly off. Nevertheless, the composition of two separated phases is always inclined toward

the composition of the two stable compounds. The degree of inclination rests upon the rate of cooling of the molten bulk body.

The experiments showed that the calcium of calcium borosilicate glass is always rich in liquid droplets. But the compositional distribution is close to the equilibrium state. This explains that a phase separation glass containing two compositions will be enriched in the respective micro phases. This fact has led us to consider the distribution of a third element (such as Co, Ni, Cu and other colored ions) being introduced. This problem and the development of color filtered glass, light excitation glass, photo sensitive glass, photo colored glass and micro crystalline glass have a very important relationship. Based on electron microscopy and microzone analysis, the results showed that 100% of the third element introduced is enriched in the micro phase liquid droplets but not in the bulk base glass. The most familiar example is that the iron content in a high silica glass is always rich in the sodium-boron phase. Therefore, it is possible to filter off iron along with sodium and boron, resulting in minimal retention of iron in the product.

Recently, Vogel [6], based on the past and current literature, has given the following summaries:

1. A simple composition (including SiO_2 , P_2O_5 , B_2O_3 , GeO_2 and BeF_2), that is, a simple glass-forming bulk of molten glass, can duly form a homogeneous glass. The structure can be described by an irregular network structure.
2. Equivalent to a certain stable compound, that is, only with a simple structural composition of the molten glass bulk, can a homogeneous glass also form.
3. All compositions of molten glass bulk between two stable compounds have a likely tendency of moving toward phase

separation. This tendency is mainly determined by the difference between the field strength of cations in the molten bulk, the interfacial energy between different compositional micro phases and by the volume occupied by different structural components.

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4. Based upon their volume fraction occupied in the total volume, any one of the two initial phases may be either the liquid droplet phase or the bulk base phase. Mainly, when the molten system possesses equal degrees of supercooling, the formation of a linkage structure is expected at the maximum phase separation.

5. The chemical composition of a micro-phase in the binomial system tends to move toward a stable compound. The degree of inclination rests upon the extent of supercooling or stability of the structural components. Accordingly, they are respectively hinged upon chemical bondings.

6. To the phase separable glass system, the addition of a low concentration of component (i.e., third element) is by no means a statistical distribution in the existing micro phase. Based on the degree of supercooling, the added component is nearly 100% concentrated in the micro phase. This contributes to the best permutational probability, that is, the high electric charge of cations always concentrate in the phase of high anion population. However, in the homogeneous glass bulk, the distribution of the additive component is statistical.

IV. EFFECT OF PHASE SEPARATION ON THE PROPERTIES OF AMORPHOUS MATERIAL

The study of the relationship between the phase separation and the properties of amorphous materials not only helps us understand the properties of glass, but also to recognize the regularity of the phase separation. Since the phase separation

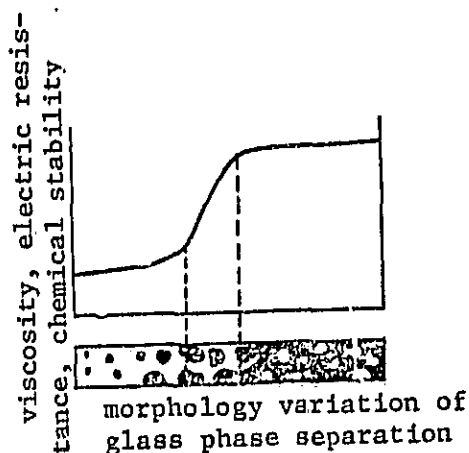


Figure 4. Effect of phase separation and its morphology on the physical properties

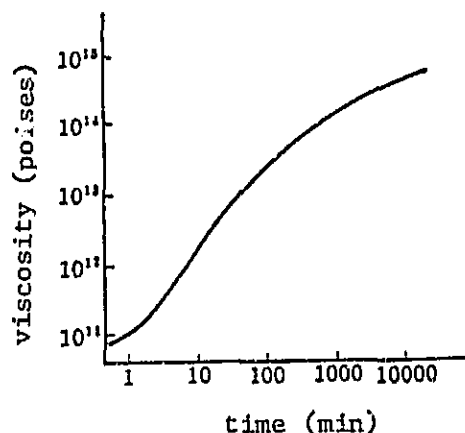


Figure 5. Measurement of viscosity vs. time at 60°C

and its morphology have more or less impact on all properties, therefore, a great deal of attention and work has been performed. On the basis of current literature, the effect of phase separation on the properties can be classified into three types:

1. Effect of phase separation on the migration characteristic properties

The migration characteristic-related properties such as viscosity, electric resistance, chemical stability and T_{13} (at temperature where viscosity is 10^{13} poises) have a significant relationship with the glass phase separation and its morphology. Мазурин and Попай-Команц [15] have used a diagram to illustrate the change of viscosity, electric resistance, chemical stability and T_{13} with the variation of morphology of the phase separation (Figure 4).

In Figure 4, the abscissa shows the variation of the phase separation morphology. The dark area indicates the high viscosity phase, high electric resistance phase or chemically stable phase. When these phases form a droplet liquid phase, the whole glass appears as low viscosity, low electric resistance or chemically

unstable. When these types of dispersed phases gradually transform into a linkage phase, the properties of glass change from low viscosity, low resistance or chemically unstable to high viscosity, high resistance or chemically stable. In other words, these properties are determined by the phase linkage of the separating phases in glass. Li and Uhlmann [16] in the study of a popular system of $0.14\text{Na}_2\text{O} \cdot 0.86\text{SiO}_2$ in the 70's, obtained the same result in conjunction with observation by electron microscopy. The viscosity and resistance of glass are hinged upon whether the phase linkage is in silica rich or alkali rich phase.

The viscosity of glass having two phases with a phase linkage morphology is highly sensitive to the measuring time. Simmons [17], in his study of the relationship of sodium borosilicate glass viscosity to measuring time, gave the following result. Figure 5 shows the viscosity of glass measured with a glass wire stretching method at 600°C . As time of measurement is lengthened, the viscosity almost increases by four exponential powers. The author pointed out that these results are due to the occurrence of a coarsening effect in the course of measurement resulting in formation of a linkage between two phases. The equilibrium stage appearing after an extended measuring period is due to the phase separation process reaching its final equilibrium. /285

2. Effect of phase separation on the physical characteristics of amorphous material

The physical characteristics include density, refractive index, coefficient of expansion, elastic modulus and strength, etc. The phase separation of glass and its morphology have some effect on those properties, but not to a great extent compared to the first type. However, there is a simple rule to observe. Shaw and Uhlmann [18] pointed out that in the phase separation zone of a system, when density is plotted against composition (weight %), one will obtain a curve with a positive curvature. Based on this

the extent of phase separation in certain glass systems was predicted by the authors. Later, Topping, et al. in their study of the $\text{PbO-GeO}_2\text{-SiO}_2$ and PbO-GeO_2 systems also found the identical result when both density and refractive index of a phase separation zone were plotted against the composition. They have further verified the statement made by Shaw and his coworker.

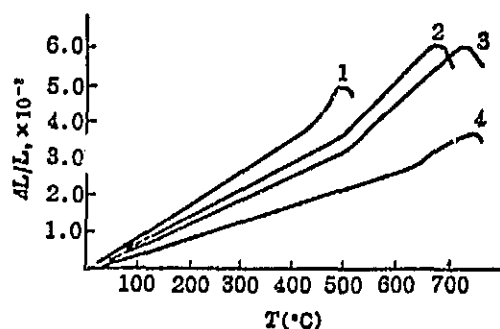


Figure 6. Effect of composition and heat treatment on thermal expansion.

The coefficient of thermal expansion of the phase separation glass mainly depends on the composition of an entire glass. Likewise, it is dependent upon the volume fraction of a phase, but is less affected by the morphology of the phase separation. This has been proved by Redwine and Field [19] in the study of the effect of a micro structure of sodium silicate glass on the physical properties. Figure 6 shows four thermal expansion curves, representing different compositions and different heat treatments. Curve 1 is the thermal expansion curve of a quenched glass containing 17.6 (g mole %) Na_2O . This represents the thermal expansion behavior of a glass with uniform nonphase separation bulk and with droplet liquid phase separation. Curve 2 contains different sodium content with 14.6% Na_2O . Curve 3 is with 12.67% Na_2O and Curve 4 with 7.2% Na_2O . Those glass systems have been annealed at 600°C for eight hours. All glass systems possess a well developed phase linkage of the separated phases. In the figure, the thermal expansion of those curves was gradually decreased due to a gradual reduction in Na_2O content. Curves 2-4 represent the thermal expansion behavior of the phase separation glasses with a linkage phase structure. Their expansion behavior above a glass transition temperature is distinguishably different from Curve 1. As far as the same glass composition is concerned, the effect of a phase separation morphology on the thermal expansion is minimal or shows nearly no effect at all, but its effect on a softening point is quite significant.

Take glass with 14.8 (g mole %) Na_2O for example; a quenched glass with uniform single phase structure shows a thermal expansion coefficient of 83.2 and a softening point of 530°C when measured at a temperature between room temperature and 350°C . As the glass is annealed at 680°C for four hours, its morphology appears as a droplet liquid phase separation, while the same one annealed at 600°C for eight hours shows a linkage phase morphology. The respective expansion coefficients are 83.6 for the former and 83.2 for the latter. Their softening points are 510°C and 665°C respectively. All these samples have identical composition but different morphologies. They display a little difference in the thermal expansion coefficients but the difference in their softening points is as great as 130°C .

3. The effect of phase separation and its morphology on glass transition temperature

When the rate of cooling is held constant, the glass transition temperature, T_g , can be regarded as the mid point of a temperature range, wherein one type of material is being transformed from a supercooled state to a glass state. The characteristic of the former state is that an ordering arrangement of atoms or ions varies with temperature, while the latter has no such variation with temperature. The glass transition temperature and viscosity of glass reflect the rate of arrangement of atoms or ions of glass under a constant temperature. Generally, glass at its glass transition temperature shows little change in viscosity; neither is the T_g is closely related to the composition of glass. For most glass material, the viscosity at T_g , η_{T_g} , is in the range of $10^{12.9}$ - $10^{13.6}$ poises. Based on the above discussion, the effect of morphology of a phase separation glass on viscosity is quite significant. The viscosity varies under a condition of whether a high viscosity phase is in linkage or scattered in the phase separation glass as shown in Figure 4. However, T_g is related to either a low viscosity phase or a high viscosity phase, particularly when

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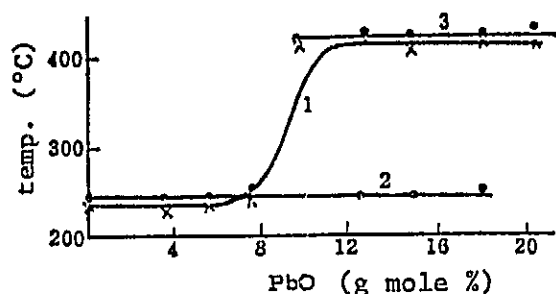


Figure 7. Relationship composition and properties of the phase separation lead borate glass.

1-- T_{13} ; 2-- T_g (low viscosity phase); 3-- T_g (high viscosity phase).

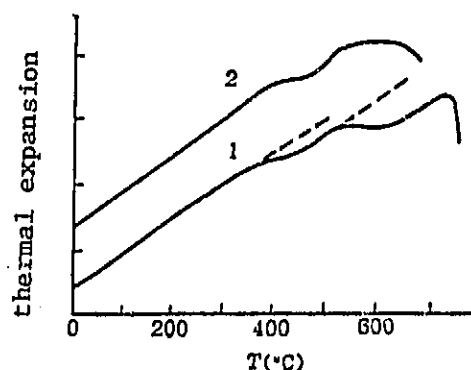


Figure 8. Two glass transition temperature of the phase separation lead borate glass (10 PbO·20 GeO₂·70 SiO₂)

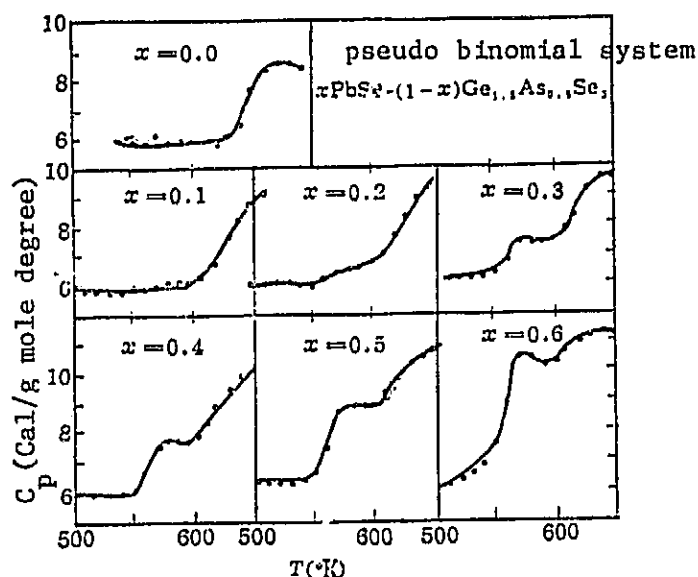


Figure 9. Heat capacity vs. temperature curves of the PbSe-Ge_{1.5}As_{0.5}Se₃ glass at glass transition zone

the high viscosity phase is a linkage phase. Masypun, et al., [20] had found two T_g 's in their study of lead borate glass as shown in Figure 7. Curve 1 is T_{13} ; curves 2 and 3 are the T_g s of low viscosity phase and high viscosity phase respectively. Topping [21] and coworkers also found two T_g s in the study of PbO-GeO₂-SiO₂ system. The glass transition temperatures were observed from the thermal expansion curves in Figure 8. The authors also pointed out that the plateau in the T_g zone is also the characteristic of a phase separation of glass. Moynihan [22], et al., in studying the relationship between heat capacity of glass and temperature of the $x\text{PbSe}-(1-x)\text{Ge}_{1.5}\text{As}_{0.5}\text{Se}_3$ system also discovered double T_g s when the PbSe concentration was increased (Figure 9). They also observed those phase separations in the glass through a transmission electron microscope. Clearly, the glass transition temperature can be measured by numerous physical property related temperature coefficients. Again, double or triple glass transition temperatures are the indication of glass phase separations. The

measurement of double T_g s by means of the thermal expansion method is quite convenient. However, in some glass systems, due to an interference by softening point, the detection of the T_g at high temperature becomes impossible.

V. THE RELATIONSHIP BETWEEN THE PHASE SEPARATION AND CRYSTALLIZATION OF AN AMORPHOUS MATERIAL

In recent years, regardless of numerous studies made on the relationship between the phase separation and crystallization of an amorphous material, there is still quite a vagueness in defining this relationship. Many researchers discovered that in certain glass systems nucleation of crystal is always preceded by a phase separation. Thus, it is considered that a phase separation promotes the crystallization and many assumptions are being made to explain their relationship [23]. Several possible functional mechanisms are summarized as follows:

1. Phase separation provides a driving force for the nucleation of crystal which is not possessed by a single phase liquid. This possibility is present in a certain system under a constant heat treatment. Zarzycki [24] used Cahn's [25] results in discussing the relationship between the phase separation and crystal nucleation. Figure 10 shows the thermodynamic aspect of a stable phase crystallization in conjunction with a phase separation. From Figure 10, the component C_0 crystallization from a spinodal liquid phase C to a solid phase C_s is impossible, because it should raise a free energy A_1B . If the spinodal phase L separates into two equilibrium liquid phases, then it is due to a drop in the free energy A_2B , which makes the dry-crystallization of C_s possible. This mechanism is particularly suitable to the case that the composition of a solid phase is far different from the composition of the separating phase. /287

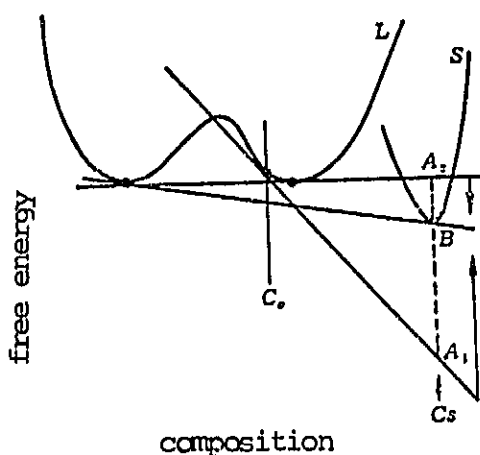


Figure 10. Variation of solid phase C_s thermodynamics potential barrier

2. Due to the generation of an interface in the separating phase, which provides a preferable nucleating site for the nucleation of a crystalline phase. Under normal circumstances, this type of the crystalline phase nucleation is not observed. This is probably due to very small interfacial energy between the two liquid phases. Hammel [26] measured the interfacial energy of the two liquid phases in the $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ system and found that the interfacial energy is less than 5 ergs/cm^2 . Normally, the interfacial energy between liquid phase and crystalline phase is in the range of $50-200 \text{ ergs/cm}^2$. Therefore, it seems difficult to expect that the interface of two liquid phases can provide a preferable site for the nucleation of a crystalline phase.

However, in some circumstances, it is possible to see a nucleation promoted by the phase separation. The resulting new phase grows on the surface of the single phase. Bando [27], et al. pointed out that in a $\text{Li}_2\text{O} \cdot 2.6\text{SiO}_2$ (g mole) system containing 0.1 (weight %) of Ag_2O , the nucleation of Ag occurs in the silica rich interface. The authors considered that Ag^+ ions in the glass structure behave like a modifier similar to Li^+ ions. When this type of glass is heated above its glass transition temperature, it separates into silica rich and lithium rich phases. Therefore, all modifier ions will be separated from the silica rich phase as shown in Figure 11, because Ag^+ ion compared to Li^+ ion has a

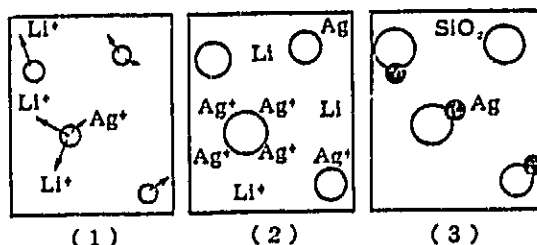


Figure 11. Ag nuclei formation process promoted by phase separation.

larger mass, greater polarity and stronger covalency. It coherently combines with oxygen atoms of the tetrahedral SiO_4 . Thus, the rate of diffusion of the A_g^+ ions from the silica rich droplet liquid phase to the bulk base phase is much slower than that of the Li^+ ions. Consequently, during the phase separation of glass, the concentration of A_g^+ ions is higher than Li^+ ions on the surface of silica rich liquid droplets as shown in Figure 11(2). Based on the result reported by Nakagawa [28], et al., that in $\text{LiO}_2\text{-SiO}_2$ glass with a large quantity of TiO_2 , the formation of lithium titanate crystal frequently occurs at the surroundings of the silica rich phase. The surface of the droplet liquid phase becomes a uniform nucleating site. Likewise, Bando and coworkers recognized the similar situation that A_g^+ ions after being reduced to A_g^0 will gradually coalesce together to form a nucleus on the surface of the silica rich droplet phase as illustrated in Figure 11(3).

3. Even in a very large supercooled zone, the phase separation will cause in the emerging phase a considerably greater atomic migration rate compared to the mother phase (bulk homogeneous phase). This high migration rate is able to promote a uniform nucleation in the system. But under a supercooling temperature, it may only allow a heterogeneous nucleation in the mother phase. On the basis of these considerations, for a certain system, the major function of a phase separation with the development of a crystalline phase nucleation may be due to the formation of a dispersed phase with a high atomic migration rate. This dispersed phase may be either a low viscosity or high viscosity phase [29]. If a high viscosity dispersed phase with a size of 3 nm in diameter is suspended in the low viscosity phase (normally in many micro crystalline glass systems, β -quartz solid solution is an emerging crystalline phase), then 1/5 of molecules of the dispersed droplet liquid phase will be in the surface layer of the droplets. Thus, the structure of the dispersed phase can be altered easily. When the structure of an outer layer is altered, this further stimulates the alteration of the structure of the next inner layer.

As a result, the overall rate of altering the crystalline structure is greatly accelerated. Even though the nucleation of crystal within the separated phase may be a heterogeneous nucleation, the presence of a fairly high molecular migration zone is still important.

4. The phase separation causes the nucleating agent to accumulate in one of the two phases. The nucleating agent enriched phase will change from the liquid phase into a crystalline phase and the nucleation occurs. A general mechanism of this type can be seen from the following works.

The function of certain oxides such as TiO_2 , ZrO_2 and P_2O_5 toward the crystallizing nucleation of glass is still unclear. Take TiO_2 containing aluminum silicate, for instance; the role of TiO_2 is whether to promote a phase separation or the formation of a phase particularly rich in TiO_2 . This is a worthy problem for study. Doeherty [30], et al., in their study of 9608 microcrystalline glasses, found that two glass systems having the same composition but with or without the presence of TiO_2 component give about 50 Å size of phase separation for both systems during the molten glass cooling process. However, the one containing 4.75% TiO_2 had an $\text{Al}_2\text{Ti}_2\text{O}_7$ nucleus appearing initially after a heat treatment. The size of the nucleus is about 50 Å. The continued heat treatment had resulted in the formation of β -petalite microcrystalline glass, which was finally transformed into β -spodumene with a small amount of rutile microcrystalline glass. On the other hand, the glass without TiO_2 also showed a phase separation during a cooling process. A continued heating of this glass only the surface nucleation was observed. The crystallization of an entire bulk body started only when the TiO_2 concentration had reached 2.5%. At this point, the formation of aluminum titanate was detected. The formation of these nuclei always preceded the appearance of petalite. Therefore, it is regarded that the formation of the $\text{Al}_2\text{Ti}_2\text{O}_7$ nuclei is unquestionably

affected by the phase separation. But one phase of the phase separation glass is TiO_2 rich phase, which forms a nucleus during the heat treatment. This has been supported by observation through a transmission electron microscope.

Neilson [31] in the study of nucleation and crystallization behaviors of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-ZrO}_2$ system by means of the small angle X-ray scattering (SAXS) explained that there is a ZrO_2 micro zone of 50 Å formed in a certain glass. When the zone underwent a heat treatment at 850°C for different time durations, the zone was not enlarged but the concentration of ZrO_2 increased. The sufficient number of ZrO_2 micro zones may be considered as the crystallized nuclei of a high temperature quartz. In a certain glass system, ZrO_2 also crystallizes out, but it has nothing to do with the crystallization of the high temperature quartz. Thus, this type of glass does not have a specific nucleation step.

From the above examples, the component of a nucleating agent of glass is always accumulated in one phase of the phase separation glass. It seems apparent that when these components are enriched to a certain degree, those micro zones (50 Å) will be transformed from an amorphous state to a crystalline state and the nucleation takes place. However, some problems have remained unanswered such as the synergistic function between TiO_2 and ZrO_2 and the detailed structure of a glass phase separation prior to the crystallizing nucleation of glass; these require further clarification.

A great deal of study has been done on the $\text{LiO}_2\text{-SiO}_2$ system without the addition of a nucleating agent. However, few affirmative suggestions were obtained with regard to the relationship between the phase separation and crystallizing nucleation. Some works [27,32] revealed a very significant effect of a phase separation on the nucleation. But the others [28,33] were inconclusive. Likewise, the study of the crystallization behavior of the

$\text{LiO}_2\text{-SiO}_2$ glass system with different nucleating agents also yielded little encouraging result concerning the additives.

Similar controversial results were obtained with regard to the relationship between the phase separation and a crystal growth. Harper's [33] results indicated that the glass phase separation changes a crystal growth rate. Tomozawa [34] pointed out that the phase separation of glass changes the activation energy of crystal growth. A higher activation energy of the crystal growth (82.5 Kcal/g mole) was obtained for a glass was found. out the phase separation, while a lower activation energy of crystal growth (54 Kcal/g mole) for the phase separation glass. However, other reports indicated that the phase separation has no effect on the dynamics of crystal growth.

In conclusion, the relationship between the phase separation and the growth of a nucleating crystal is a very complex yet a vague problem. However, it is particularly significant if the phase separation is considered as a process of promoting the transformation of an amorphous state into a crystalline state.

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